ECO–FRIENDLY OXIDIZERS: MINIREVIEW

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***Abstract**: In order to protect the environment, today's legislation encourages the development of materials, substances and so on, which can lead to a minimum harmful effect. As a result, the concept of eco-friendly makes its appearance and begins to occupy a leading place on the working boards of engineers from different fields of aerospace engineering as well as in the field of mechanical engineering (such as fertilizers, building materials, energy generation, and so on).This paper aims to go through the existing literature up to the present moment regarding the stage of development of environmentally friendly oxidants, which can be found in the specific structure of a solid propellant.*

***Keywords**: Propellant, Eco-friendly oxidizers, Ammonium perchlorate, Ammonium nitrate, Ammonium dinitramide, Hydrazinium nitroformate.*

Introduction

Analyzing the environment, more precisely, the level of pollution that is achieved by using excessively and improperly the materials that favor its growth, we can conclude only one sure aspect, the concept of eco-friendly must become an imperative one.

Starting from the typical structure of a solid propellant for rocket engines: fuel, oxidant and binder, all these elements put together must meet the three requirements that a product must present: safety, performance and financial part. When it comes to environmentally friendly propellants we refer to those constituents that are used in their manufacture, which, during the combustion develop products that have a minimal harmful effect on the ecosystem, but at the same time confer at least equal performances with those that exist on the market at the moment, preferably even to exceed them.Reduced performance would lower payloads and increase propellant consumption, and thereby have a negative impact on the environmen. From the point of view of the mass proportions of a solid rocket fuel, the oxidant is the vital element, it is the center of the mixture and the others gravitate around it to fulfill the requirements specified above. Usually this is the basis of the eco-friendly character.

The development of eco-friendly propellants represents at moment the most coveted aspect that aerospace engineers want to achieve, by identifying new oxidants capable of successfully replacing non-environmentally friendly oxidants, such as ammonium perchlorate. Good candidate compounds for green high performance propulsion are amonium nitrate (AN), hydrazinium nitroformate (HNF), and ammonium dinitramide (ADN). They are being studied as eco-friendly oxidizers for future solid propellants with improved properties.[1-6, 21]

1. Non-environmentally friendly versus environmentally friendly

Combustion products are an important issue that we must take into account when it comes to environmental protection. Usually, gaseous products and solid residues are to be determinated.

Regarding the non-evironmentally friendly oxidants, the bigest candidate it is represented by ammonium perchlorate (AP). Its structure is shown in Figure 1.

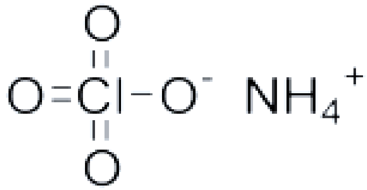


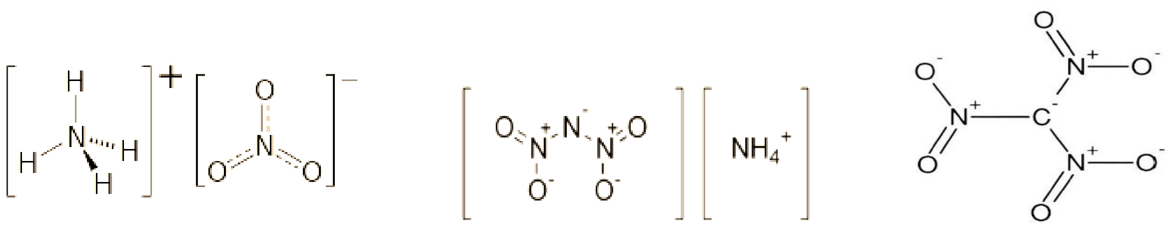
Figure 1: Structure of ammonium perchlorate[7]

Despite its non-ecofriendly character, history and specialized studies[8-12] have shown us that ammonium perchlorate is the most effective oxidant in terms of aerospace performance. Its efficiency is related to the burning rate. However, it does possess a series of major disadvantages that bring him a leading position on the black board of non-environmentally friendly oxidants. Figure 2 describes its decomposition reaction, where it can be easily observed among the reaction products (nitrogen, oxygen, and water), the appearance of hydrogen chloride, which in contact with water leads to the formation of hydrochloric acid. This type of acid produces smoke and is highly toxic, in addition to the corrosion of the launch pad. Also, the reaction products have a negative effect on the ozone layer which increases the global warning.

$$4\ NH_4ClO_4 \rightarrow 4\ HCl + 2\ N_2 + 5\ O_2 + 6\ H_2O$$

Figure 2: Decomposition reaction of ammonium perchlorate [13,14]

In order to overcome these environmental problems, specialists in the field have begun to identify new compounds capable of successfully replacing ammonium perchlorate but to present at least the same characteristics in terms of thermodynamic / energetic, kinetic, and physico-chemical properties. Among these oxidants are ammonium nitrate, ammonium dinitramide and hydrazinium nitroformate (Figure 3), which are currently studied extensively.



a **b** **c**

Figure 3: Structure of AN (a), ADN (b), HNF (c)

The eco-friendly character that these three posess results from the decomposition reactions shown in Figure 4.

$$2\ NH_4NO_3 \rightarrow 4\ H_2O + 2\ N_2 + O_2$$

$$NH_4N(NO_2)_2 \rightarrow (2NH_2NO_2) \rightarrow 2N_2O + 2H_2O$$

$$\mathrm{HNF} \longrightarrow 2\,\mathrm{NO} + \mathrm{CO_2} + 2\,\mathrm{H_2O} + 3/2\,\mathrm{N_2} + 1/2\mathrm{H_2}$$

Figure 4: Decomposition of AN, ADN and HNF

Although, ammonium nitrate is a conventional oxidant without non-eco products, this one has drawbacks of hygroscopic nature and multiple transition phases in the temperature range of practical importance and comparatively lower energy. Therefore, related studies on ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) as potent candidates regarding eco-friendly oxidants are developed all over the globe. Related to the last two, HNF has certain advautages over ADN, such as its simple method of synthesis, non-hygroscopic nature, higher density and melting point[18].

Considering the structure of a solid rocket propellants in addition to the oxidant, there are also other elements such as the binding agent. The main purpose of this kind of agent is to hold together in a matrix the mixture. The necessity of development of solid rocket propellants based on ammonium nitrate, ammonium dinitramide and hydrazinium nitroformate more energetic led to the emergence energetic binders, such as glycidyl azide polymer (GAP), polyglycidyl nitrate (PGN), polynitromethyloxetane (PLN) and 3,3-bis(azydomethyl)oxetane (BAMO).

A theoretical study regarding the energetic was conducted by G. Gadiot et al[20]. In this study, a series of combinations eco-friendly oxidants and energy binders were made. The mass percentages used were 80% for oxidants and 20% for binder. The Table 1 lists the theoretical maximum perfomance for selected smokelles solid propellants obtained in this study.

Oxidizer (% by weight)	Fuel (% in weight)	Maximum I_{vac} (m/s)	Gain in I_{vac}† (%)	Flame temperature, T_f (K)	Increase in T_f (%)
80% AP*	20% HTPB	2713	—	2266	—
80% AN	20% HTPB	2412	−11.1	1420	−37
80% AN	20% GAP	2717	+0.2	2353	+4
80% ADN	20% GAP	3150	+16.1	3132	+38
80% HNF	20% GAP	3278	+20.8	3275	+45
80% ADN	20% PGN	2938	+8.3	2900	+28
80% HNF	20% PGN	3282	+21.0	3318	+46
80% ADN	20% PLN	3111	+14.7	3018	+33
80% HNF	20% PLN	3306	+21.9	3321	+47
80% ADN	20% BAMO	3175	+17.0	3139	+39
80% HNF	20% BAMO	3255	+20.0	3381	+49

*Reference propellant.
†Gain with respect to reference propellant.

Table 1: The theoretical maximum perfomance for 80% oxidiant and 20 % binder

Propellants are designed to produce high temperatures and pressures in a closed chamber to accelerate projectiles, rockets, or missiles by means of the resulting propulsive force of the gas produced by its decomposition (burn). As it can be seen, the green oxidants can give good results using them in different combinations with another material.

Even if the energetic problem is overcome, the majority of oxidants present other problems too.

For instance ammonium nitrate, besides the low energetics, this one is also very hygroscopic, undergoes a room temperature phase transformation (see Table 2), involving a significant volume change and burns very slowly.These adverse properties make it even less attractive as an alternative oxidizer. From here the concept of phase stabilized ammonium nitrate (PSAN) becomes known.

Phase transition	Temperature (°C)	State	Volume variation (%)
-	>169.6	liquid	-
I	169.6 to 125.2	cubic	+2.1
II	125.2 to 84.2	tetragonal	-1.3
III	84.2 to 32.3	α-rhombic	+3.6
IV	32.3 to −16.8	β-rhombic	−2.9
V	−16.8	tetragonal	-

Table 2: Ammonium nitrate phase transition [21]

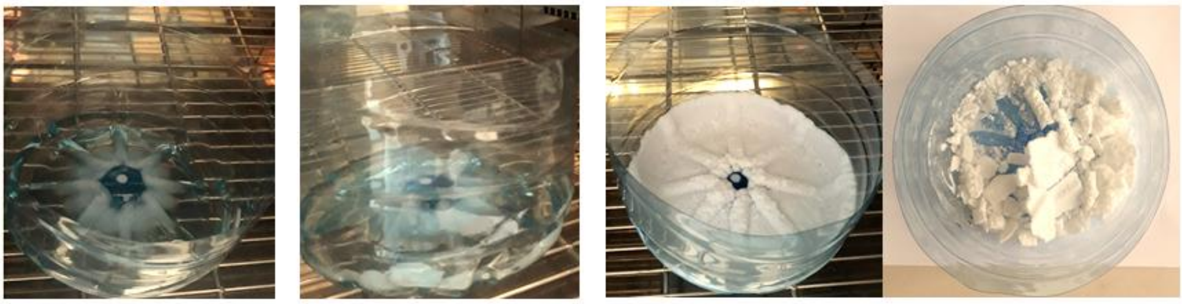
2. Phase trasition. Experimental study regarding ammonium nitrate

2.1 Materials

To obtain the desired phased stabilized ammonium nitrate desired, the following materials were used: ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3) and distillated water as a solvent.

2.2 Co-crystallization process

It was made a mixture of ammonium nitrate and potassium nitrate (PN), using distillated water as a solvent agent. The quantities used in the experiment were: 47,5 grame ammonium nitrate, 2,5 grame potassium nitrate and 100 ml distillated water (DW). After weighing and measuring using an analytical balance and a graduated cylinder the mixture was placed in a 600 ml Berselius glass placed on a magnetic agitator. The dissolving process of the two salts in the 100 ml of distilled water took 3 hours, with a rotational speed of the magnetic agitator of 500 rpm. After the total dissolving the obtained mixture was placed in a plastic vessel to be subsequently introduced into a ventilation drying stove. The mixture was dried at a temperature of 50-80^{o} C for water evaporation. The total duration of the process was 72 hours, and the obtained compound consisted in a salt of ammonium nitrate and potassium nitrate (see Figure 4). The co-crystallization reaction was successfully performed. All the stages regarding the completion of the co-crystallization reaction are presented in the Figure 5.



24 h 36 h +72 h

Figure 5: Ammonium nitrate-potassium nitrate salt

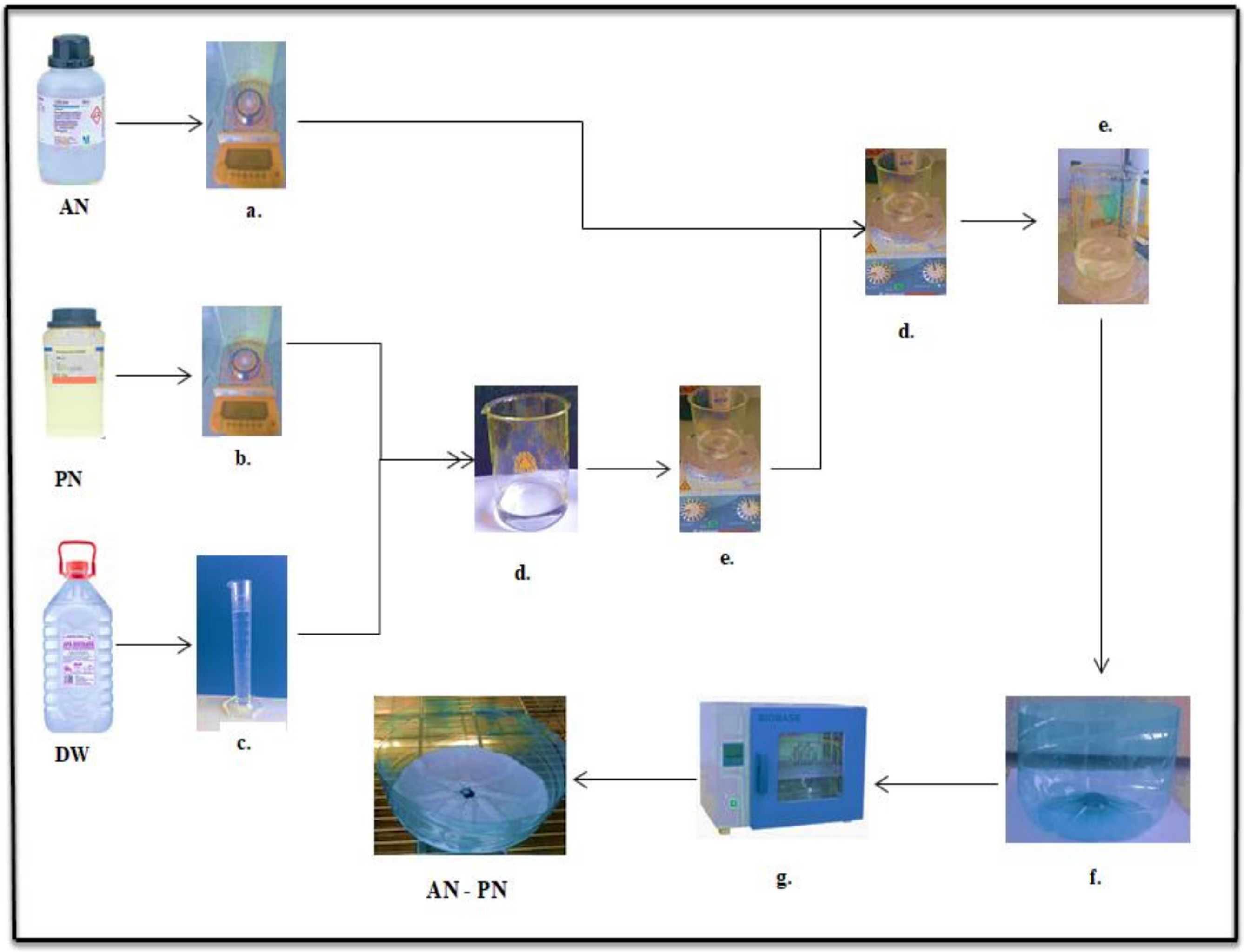


Figure 6: Process of co-crystallization ammonium nitrate-potassium nitrate
(a,b- weighing; c- measuring; d- mixture; e- dissolving; f-sampling; g-drying)

For proper storage the salt obtained was disposed in a vacuum desiccator during the laboratory tests.

2.3 Characterisation

After the salt is obtained, the next step is to check the stability of the ammonium nitrate by a differential thermal analysis to see if it is PSAN. The tests of the samples were carried out using a DTA 551-Ex model, by employing a heating rate of 5^{O} C. The sample size used was about 30 mg.

The reported transition temperatures for various phases of AN are shown in Table 2. Since the transition depends on the purity of the sample, AN used was characterized using the same experimental conditions, as the same for the PSAN used in the present study. Figure 7 shows all the transitions phase from the room temperature upwards as expected from an untreated sample. The IV-III transition occurs 42^{O} C instead of 32^{O} C, wich is not unusual since this transition is known to take place anywhere between 32 and 80^{O} C depending on the source of the sample. After this transition, the sample has three more transitions before decomposing endothermically above 300 ^{O} C.

At a close look to the PSAN phase transitions it can be observed that the transition which normally occurs at 42^{O} C, in case of AN, had vanished by using potassium nitrate in the process of co-crystallization. The co-crystalization is believed to cause formation of solid solution of K^{+} salts in AN[19].

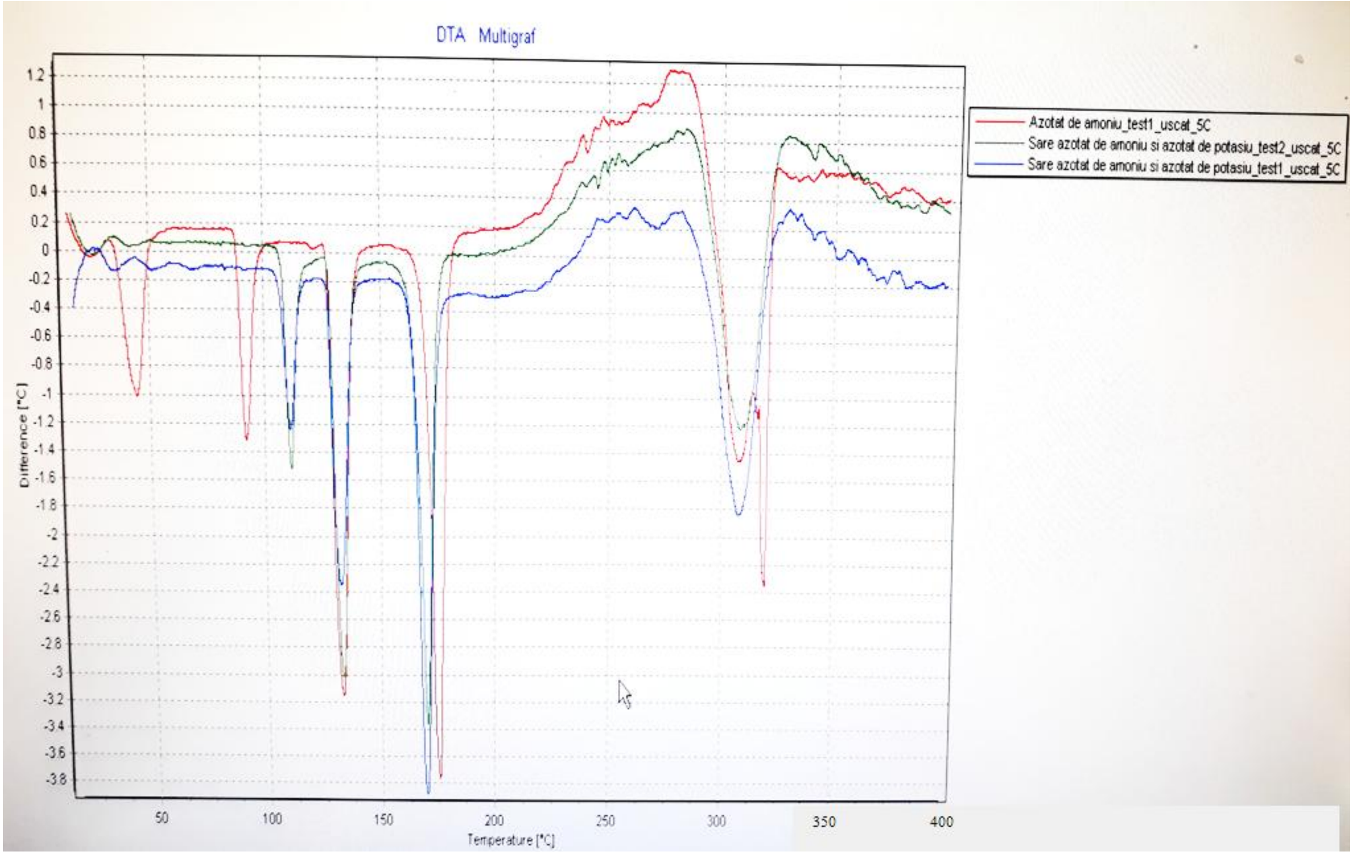


Figure 7: DTA traces on AN and PSAN

3. Conclusions

In conclusion, composite solid propellants based on oxidants such as ammonium nitrate or ammonium dinitramide and hydrazinium nitroformate possess good characteristics regarding eco-friendly character. However, these oxidants have a low response when it comes to performance and most of the time they have to be used with other components, such as energetic binders to improve their characteristics. Taking into consideration all the factors, the eco-friendly oxidants are the next step wich can be used as an alternative to AP composite solid propellants.

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